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**Status of Final Reports**

Enclosed is a copy of the final technical report for AFOSR grant F49620-96-1-0249,  
Dr. Steven George, P.I.

Should you have questions or you need additional information, I may be contacted at  
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A handwritten signature in black ink that appears to read "Jan Farrar".

Jan Farrar - Reports Coordinator

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<b>13. ABSTRACT</b> (Maximum 200 words) <p>The ASSERT research projects that have focused on thin film growth on various substrates examined the adsorption and desorption kinetics of tetrakis and dimethylamine on TiN surfaces. The competition between TDMAYT and DMA for surface sites during TiN growth with TDMAAT is a model system to understand reaction product inhibition that affects the conformal deposition of TiN. Studied the adsorption and decomposition of 1,4-disilabutane (DSB) and porous silicon surfaces. DSB is a possible new precursor for SiO<sub>2</sub>, SiC and Si growth. Explored atomic layer controlled chemical vapor deposition methods to deposit oxide and nitride thin films. Most of this work concentrated on Si<sub>3</sub>N<sub>4</sub> deposition and the catalytic deposition of SiO<sub>2</sub> at room temperature using ellipsometry techniques to monitor the film growth. Evaluated the conformality and surface roughness of Si<sub>3</sub>N<sub>4</sub> and SiO<sub>2</sub> films deposited with atomic layer controlled growth methods using atomic force microscopy (AFM) techniques. Studies the surface chemistry occurring during the chemical vapor deposition (CVD) of ZrO<sub>2</sub> using tetra-tert-butoxy-zirconium (ZTB) as the molecular precursor. Examined ZrO<sub>2</sub> films deposited using ZTB as the molecular precursor using AFM and Auger electron spectroscopy depth profiling. Utilized SiO<sub>2</sub>, TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> atomic layer growth techniques to reduce pore diameters in porous membranes. This controlled reduction in pore size is important for fabricating a molecular sieving membrane for gas separation applications. Another achievement of the research is the education of students. Several students were funded with the support through the ASSERT program. A former graduate student who continued to work as a post-doctoral fellow in the research group, also contributed to this ASSERT effort.</p>				
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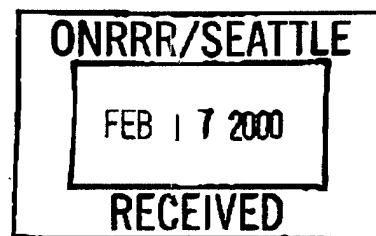
*Final Report*

**Ceramic Coatings on Metals Using Atomic  
Layer Controlled Chemical Vapor Deposition  
(ASSERT-96)**

AFOSR Grant No. F49620-96-1-0249

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## I. Program Objectives

Our support through the ASSERT program has focused on ceramic coatings deposited using new atomic layer controlled chemical vapor deposition methods. Ceramic coatings on metal are extremely important to prevent the corrosion and to improve the thermal resistance of metals at high temperature. One important example is ceramic coating on nickel superalloy surfaces of an aircraft gas turbine engine. This coating helps to prevent metal oxidation and corrosion at the high engine exhaust temperatures. The adhesion of ceramic coatings on the metal surface is also crucial for their optimum performance.

Our ASSERT research focused on the deposition of oxide and nitride thin films that can be utilized to protect surfaces from corrosion and high temperature damage. This research explored novel chemical vapor deposition methods to grow optimized ceramic coatings. One approach was to utilize atomic layer controlled (ALC) chemical vapor deposition (CVD) techniques by employing self-limiting surface reactions. The films deposited using ALC-CVD techniques may be much more conformal and higher quality than films deposited using conventional CVD approaches. A second approach developed new chemical vapor deposition techniques to deposit  $ZrO_2$  thermal barrier coatings.  $ZrO_2$  is a refractory ceramic and has excellent resistance at high temperatures and various chemical conditions.

Our research utilized a variety of techniques to study the surface chemistry of oxide deposition and to measure the growth of oxide films. Fourier transform infrared (FTIR) spectroscopy was used to analyze the surface species during chemical vapor deposition. These FTIR studies allowed us to evaluate the surface chemistry and to determine the optimum conditions for thin film growth. Spectroscopic ellipsometry was also utilized to measure thin film thicknesses and their refractive indices. These ellipsometric measurements allowed us to quantify growth rates and evaluate the quality of the films.

## II. Program Achievements

Our ASSERT research projects that have focused on thin film growth on various substrates. A list of our accomplishments is given below:

- Examined the adsorption and desorption kinetics of tetrakis(dimethylamino)titanium (TDMAT) and dimethylamine (DMA) on TiN surfaces. The competition between TDMAT and DMA for surface sites during TiN growth with TDMAT is a model system to understand reaction product inhibition that affects the conformal deposition of TiN.

- Studied the adsorption and decomposition of 1,4-disilabutane (DSB) ( $\text{SiH}_3\text{CH}_2\text{CH}_2\text{SiH}_3$ ) on  $\text{Si}(100)2\times 1$  and porous silicon surfaces. DSB is a possible new precursor for  $\text{SiO}_2$ ,  $\text{SiC}$  and  $\text{Si}$  growth.

- Explored atomic layer controlled chemical vapor deposition methods to deposit oxide and nitride thin films. Most of this work concentrated on  $\text{Si}_3\text{N}_4$  deposition and the catalytic deposition of  $\text{SiO}_2$  at room temperature using ellipsometry techniques to monitor the film growth.

- Evaluated the conformality and surface roughness of  $\text{Si}_3\text{N}_4$  and  $\text{SiO}_2$  films deposited with atomic layer controlled growth methods using atomic force microscopy (AFM) techniques.

- Studied the surface chemistry occurring during the chemical vapor deposition (CVD) of  $\text{ZrO}_2$  using tetra-tert-butoxy-zirconium (ZTB) as the molecular precursor.

- Examined  $\text{ZrO}_2$  films deposited using ZTB as the molecular precursor using AFM and Auger electron spectroscopy depth profiling.

- Utilized  $\text{SiO}_2$ ,  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$  atomic layer growth techniques to reduce pore diameters in porous membranes. This controlled reduction in pore size is important for fabricating a molecular sieving membrane for gas separation applications.

Another achievement of the research is the education of students. Several students were funded with our support through the ASSERT program. The ASSERT program partially supported the graduate research of Michelle Cameron, Jason Klaus, Lynn Okada and Ian Gartland. Brian Berland, a former graduate student who continued to work as a post-doctoral fellow in the research group, also contributed to this AASERT effort.

All of these graduate students now have jobs. Michelle Cameron graduated in December 1999 and is now employed at Rocky Flats in Golden, Colorado. Jason Klaus graduated in June 1999 and is now employed at Intel in Hillsboro, Oregon. Lynn Okada graduated in December 1997 and is now employed at Advanced Micro Devices in Sunnyvale, California. Ian Gartland graduated with a Masters and is now employed at Eltron Research in Boulder, Colorado. Brian Berland is now a staff scientist at ITN Energy Systems in Wheat Ridge, Colorado.

### III. New Results from AFOSR Support

We studied the adsorption and desorption kinetics of tetrakis(dimethylamino)titanium (TDMAT) and dimethylamine (DMA) on TiN surfaces. This study revealed the competition between TDMAT and DMA for adsorption sites on the TiN surface. Because DMA is a reaction product of TDMAT decomposition, this competition may explain the nonconformal deposition of TiN using TDMAT on high aspect ratio structures.

We also studied the adsorption and decomposition of 1,4-disilabutane (DSB) ( $\text{SiH}_3\text{CH}_2\text{CH}_2\text{SiH}_3$ ) on  $\text{Si}(100)2\times 1$  and porous silicon surfaces. DSB is a potential precursor to deposit Si,  $\text{SiO}_2$  or  $\text{SiC}$ . We observed an interesting decomposition pathway where Si species and ethylene adsorb to the silicon surface. The ethylene can then desorb to leave only Si deposited on the silicon surface. The ethylene desorption removes the carbon species and prevents the stoichiometric deposition of  $\text{SiC}$ .

We also examined the atomic layer control of  $\text{Si}_3\text{N}_4$  films. Using atomic layer controlled growth methods, we demonstrated the deposition of  $\text{Si}_3\text{N}_4$  films with atomic layer precision on  $\text{Si}(100)$  and porous silicon surfaces. These  $\text{Si}_3\text{N}_4$  films may be useful as higher dielectric constant insulating layers in thin film devices.

We also demonstrated the conformal deposition of  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$  and  $\text{TiO}_2$  on very high aspect ratio pores in porous alumina membranes. These oxide coatings may be important to protect the porous alumina membrane. In addition, the atomic layer deposition of  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$  and  $\text{TiO}_2$  can selectively reduce the pore diameter and help to separate gases by molecular sieving.

Using tetra-tert-butoxy zirconium (ZTB) [ $\text{Zr}(\text{O}(\text{CH}_3)_3)_4$ ] as the molecular precursor, we also examined the surface chemistry during  $\text{ZrO}_2$  deposition and the characteristics of the deposited  $\text{ZrO}_2$  film. Ellipsometric studies of  $\text{ZrO}_2$  film growth explored the deposited  $\text{ZrO}_2$  film thickness versus substrate temperature for constant ZTB exposure. No  $\text{ZrO}_2$  film growth was observed until  $T>600\text{K}$ . The  $\text{ZrO}_2$  film growth then increased nearly exponentially versus temperature and reached the maximum growth rate at 700-800 K.  $\text{ZrO}_2$  film thicknesses of  $\sim 2500$  Å were deposited at 700 -800 K in 3600 s at a ZTB pressure of 0.05 Torr.

The  $\text{ZrO}_2$  films were also examined using Auger electron spectroscopy (AES) sputter-depth profiling methods. The films contained almost entirely Zr and O. Only very small  $<1\text{-}2\%$  levels of carbon contamination were observed by AES analysis. At higher growth temperatures  $T>800\text{ K}$ , the  $\text{ZrO}_2$  film growth rates decreased dramatically and showed high carbon contamination. These results suggest that pyrolysis of the ZTB precursor may be a problem at these higher temperatures.

#### IV. Personnel Supported

##### *Graduate Students*

1. Michelle Cameron
2. Jason Klaus
3. Ian Gartland
4. Lynn Okada

##### *Postdoctoral Research Associates*

1. Dr. Brian Berland (former PhD in research group)

#### V. Publications

J.W. Klaus, O. Sneh and S.M. George, "Atomic Layer Controlled SiO<sub>2</sub> Growth at Room Temperature using Catalyzed Binary Reaction Sequence Chemistry", *Science* **278**, 1934 (1997).

L.A. Okada, A.C. Dillon, A.W. Ott and S.M. George, "Adsorption and Decomposition of 1,4-Disilabutane (SiH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>SiH<sub>3</sub>) on Si(100)2x1 and Porous Silicon Surfaces", *Surface Science* **418**, 353 (1998).

J.W. Klaus, A.W. Ott, A.C. Dillon and S.M. George, "Atomic Layer Controlled Growth of Si<sub>3</sub>N<sub>4</sub> Films Using Sequential Surface Reactions", *Surface Science* **418**, L14 (1998)

B.S. Berland, A.W. Ott, I.P. Gartland and S.M. George, "In Situ Monitoring of Atomic Layer Controlled Pore Reduction in Microporous Alumina Membranes Using Sequential Surface Reactions", *Chemistry of Materials* **10**, 3941 (1998).

L.A. Okada and S.M. George, "Adsorption and Desorption Kinetics of Tetrakis(dimethylamino)titanium and Dimethylamine on TiN Surfaces", *Applied Surface Science* **137**, 113 (1999).

M.A. Cameron and S.M. George, "ZrO<sub>2</sub> Film Growth by Chemical Vapor Deposition Using Zirconium Tetra-tert-Butoxide", *Thin Solid Films* 348, 90 (1999).

We have also submitted another manuscript for publication. This manuscript is currently being reviewed and we hope for its publication sometime in 2000.

M.A. Cameron, I.P. Gartland, J.A. Smith, S.J. Diaz and S.M. George, "Atomic Layer Deposition of SiO<sub>2</sub> and TiO<sub>2</sub> in Alumina Tubular Membranes: Pore Reduction and Effect of Surface Species on Gas Transport", submitted to *Langmuir*.

## VI. Interactions/ Transitions

We have had many industrial interactions as a result of this research. We have had an ongoing collaboration with Chevron because of their interest in ceramic materials for catalysis and separation processes. We have also received support from Chevron in the form of a contract that expired in November 1997.

As a result of the Chevron collaboration, we have also developed a collaboration with the CANMET Energy Technology Centre in Canada. CANMET is interested in ceramic coatings to protect and enhance the properties of their catalytic membranes. We worked under a non-disclosure agreement and modified ceramic membranes from CANMET. The results of these modifications were inconclusive.

We have talked extensively with Nanomaterials Research Corporation in Longmont, Colorado. They are making porous alumina membranes with very well-defined pore sizes. We would like to take the membranes and reduce their pore diameters to specific diameters using our atomic layer controlled growth methods. Other applications include coating nanochannel plates with films of different chemical composition to change their physical properties.

We have also had several inquiries about ZrO<sub>2</sub> chemical vapor deposition since the publication of our paper in *Thin Solid Films*. Besides being an excellent thermal diffusion barrier, ZrO<sub>2</sub> is also a high dielectric constant insulator. Some groups are considering ZrO<sub>2</sub> as a replacement for SiO<sub>2</sub> in gate oxides in MOSFET devices.

## VII. New Discoveries, Inventions or Patent Disclosures

Our discovery of the catalyzed growth of  $\text{SiO}_2$  at room temperature led to an invention disclosure and a patent filing:

J.W. Klaus, O.Sneh and S.M. George, "Method of Growing Films at Room Temperature Using Catalyzed Binary Reaction Sequence Chemistry", U.S. Patent Pending

## VIII. Honors/Awards

Prof. Steven M. George was elected as a Fellow of the American Physical Society (Fall 1997). Prof. George also received the Presidential Young Investigator Award (1988-1993), the Alfred P. Sloan Foundation Award (1988), an IBM Faculty Development Award (1988), a Dreyfus Award for Newly Appointed Faculty in Chemistry (1985) and an AT&T Award for New Faculty (1985). He was promoted to tenure as an Associate Professor of Chemistry at the University of Colorado at Boulder in 1992. He was promoted to Full Professor of Chemistry at the University of Colorado at Boulder in 1995.

Prof. George is a member of the Board of Editors of *Surface Review and Letters*. Prof. George was co-chair of the Gordon Research Conference on *Electronic Materials: Chemistry, Excitations and Processing* in July 1997 in New Hampshire. He has also served as a member of the Board of Assessment of NIST Programs, *Panel for Chemical Science and Technology*, National Research Council, from January 1993-May 1998. Prof. George was also a member of the Defense Science Study Group, Institute for Defense Analysis in Alexandria, Virginia, from spring 1989- fall 1991 and has been an alumni member from fall 1991- present.